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UC-70

**Spray Calcination/In-Can
Melting: Effluent
Characterization and
Treatment**

MASTER

M. S. Hanson

March 1980

Prepared for the U.S. Department of Energy
under Contract EY-76-C-06-1830

Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
by Battelle Memorial Institute

PNL-3109

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PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
Under Contract EY-76-C-06-1830

Printed in the United States of America
Available from
National Technical Information Service
United States Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151

Price: Printed Copy \$____*; Microfiche \$3.00

*Pages	NTIS Selling Price
001-025	\$4.00
026-050	\$4.50
051-075	\$5.25
076-100	\$6.00
101-125	\$6.50
126-150	\$7.25
151-175	\$8.00
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201-225	\$9.25
226-250	\$9.50
251-275	\$10.75
276-300	\$11.00

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CONTENTS

INTRODUCTION	1
EQUIPMENT DESCRIPTIONS	3
SPRAY CALCINATION	3
Laboratory-Scale Spray Calciner	4
Pilot-Scale Spray Calciner	6
Full-Scale Spray Calciner	6
Radioactive Pilot-Scale Spray Calciner	6
IN-CAN MELTING	10
Pilot-Scale In-Can Melter	13
Radioactive Pilot-Scale In-Can Melter	13
PROCESS OFF-GAS SYSTEMS	13
Sintered Filters	13
Nonradioactive Process Off-Gas System	19
Radioactive Process Off-Gas System	20
WASTE DESCRIPTIONS	25
CALCINE CHARACTERISTICS	26
SOURCE TERMS	31
VOLATILE FISSION PRODUCTS	31
PARTICLE SIZE ANALYSIS AND PARTICLE LOADINGS	36
GASEOUS CONSTITUENTS	47
POTENTIALLY VOLATILE NON-FISSION PRODUCTS	52
EFFLUENT TREATMENT	59
CONCLUSIONS	71

CONTENTS (Contd)

ACKNOWLEDGMENTS		73
REFERENCES		75
APPENDIX: PARTICULATE SIZE DISTRIBUTIONS FROM PILOT-SCALE SPRAY CALCINER		77

FIGURES

1	Spray Calciner	4
2	Laboratory-Scale Spray Calciner/In-Can Melter	5
3	Pilot-Scale Spray Calciner/In-Can Melter	7
4	Full-Scale Spray Calciner/In-Can Melter	9
5	Radioactive Pilot-Scale Spray Calciner/In-Can Melter	11
6	In-Can Melter	12
7	Spray Calciner Filter Assembly	14
8	Filter Permeability During Pilot-Scale Spray Calciner Operation	17
9	Filter Permeability	18
10	Flow Diagram for Non-Radioactive Process Off-Gas System	20
11	Radioactive Process Off-Gas System	21
12	Typical Spray-Calcine Particle-Size Distribution	29
13	Typical Pilot-Scale Spray Calciner Particle Size Analyzer Range	39
14	Typical Pilot-Scale Spray Calciner Particle Size Distribution from 0.35 to 0.755 μm	39
15	Typical Pilot-Scale Spray Calciner Particle Size Distribution from 0.50 to 2.75 μm	40
16	Typical Pilot-Scale Spray Calciner Particle Size Distribution from 1.00 to 7.75 μm	40
17	Typical Pilot-Scale Spray Calciner Particle Size Distribution from 2.0 to 20.0 μm	41

FIGURES (Contd)

18	Typical Pilot-Scale Spray Calciner Overall Particle Size Distribution from 0.32 to 20.0 μm	42
19	Typical Pilot-Scale Spray Calciner Mass Percent Distribution	42
20	Mass Distribution, Off Gas from Pilot-Scale Spray Calciner With Clean Filters	44
21	Full-Scale Spray Calciner Off-Gas Particle Size Distribution from 0.32 to 0.755 μm	45
22	Full-Scale Spray Calciner Off-Gas Particle Size Distribution from 0.5 to 2.75 μm	46
23	Full-Scale Spray Calciner Off-Gas Particle Size Distribution from 1.0 to 12.25 μm	47
24	Full-Scale Spray Calciner Off-Gas Particle Size Distribution from 2.0 to 20.0 μm	48
25	Full-Scale Spray Calciner Off-Gas Particle Size Distribution from 0.32 to 0.755 μm	49
26	Full-Scale Spray Calciner Integrated Off-Gas Particle Size Distribution from 0.32 to 20.0 μm	50
27	Gas Chromatograph Valving System	51
28	Laboratory-Scale Spray Calciner	56
29	Startup Condensate Concentrations	61
30	Instantaneous Ruthenium and Cesium Concentrations	64
31	Average Ruthenium and Strontium Condensate Concentrations	65

FIGURES (Contd)

32	Venturi Scrubber Ruthenium and Strontium Concentrations	66
33	Instantaneous Ruthenium Concentration, Pilot-Scale Spray Calciner Run DSS-58	66
34	Sintered Stainless Steel Filter Cross Section, 100X	67

TABLES

1	Pilot-Scale Spray Calciner Design Features	8
2	Full-Scale Spray Calciner Design Features	10
3	Defense-Waste Feed Composition	25
4	Defense-Waste Activities	26
5	Composition of Thorex Fuel-Cycle Wastes	27
6	Compositions of Six Representative High-Level Radioactive Wastes as Liquids	28
7	Physical Properties of Representative Calcined High-Level Wastes	29
8	Critical Isotope Content of High-Level Waste (HLW)	32
9	Maximum Permissible Radioactive-Release Quantities	33
10	Pilot-Scale Spray Calciner/In-Can Melter Tests	35
11	Volatile Species Decontamination Factors	36
12	Spray Calciner Operating Conditions During Particulate Analysis	43
13	FSCC-9 Mass Loadings	46
14	Full-Scale Spray Calciner Gas Concentrations	53
15	Five-Day Full-Scale Spray Calciner/In-Can Melter Mean Off-Gas Data	53
16	Full-Scale Spray Calciner/In-Can Melter 5-Day Run Off-Gas Data	54
17	Laboratory-Scale Spray Calciner Data	55
18	Effect of Calciner Temperature Set-Point on NO _x Production	55

TABLES (Contd)

19	Fluoride Losses from the Laboratory-Scale Spray Calciner	.	.	.	.	.	.	.	56
20	Glass Composition for TW-2	.	.	.	.	.	.	.	57
21	Elements Found in Off-Gas Traps	.	.	.	.	.	.	.	58
22	Typical Decontamination Factors Across Off-Gas Cleanup Devices	.	.	.	.	.	.	.	59
23	Nonradioactive Off-Gas System Ruthenium Decontamination Factors	.	.	.	.	.	.	.	60
24	Nonradioactive Off-Gas System Cesium Decontamination Factors	.	.	.	.	.	.	.	60
25	Condensate Concentrations DSS-49	.	.	.	.	.	.	.	62
26	Venturi Scrub Concentrations DSS-49	.	.	.	.	.	.	.	62
27	Packed Scrub Concentrations DSS-49	.	.	.	.	.	.	.	63
28	Gross Activity Released to Stack During Radioactive Operation	.	.	.	.	.	.	.	69
29	Radioactive Effluent System Minimum Decontamination Factors	.	.	.	.	.	.	.	69
30	WSEP Spray Solidification Data	.	.	.	.	.	.	.	69

INTRODUCTION

As experience throughout the world has been accrued with high-level nuclear waste immobilization systems, it has become obvious that a major portion of the necessary processing is and will be related to the cleaning of the off gases from these systems. A large amount of operational experience with waste immobilization, particularly vitrification, has been gained at the Pacific Northwest Laboratory (PNL).

Although the decision has not been made in the United States as to the type of waste form and process to be required, a primary contender in the field of waste immobilization is the spray calcination/in-can melting process. This process, developed over the past years at PNL, has been the subject of intense study. An area closely related to the process is that of off-gas control.

Off-gas cleanup requirements will specify the level of treatment necessary as well as the hardware to be used in immobilization facilities. These cleanup requirements primarily depend on two specifications: the source terms generated at the immobilization equipment, and the allowable release rates. This research is undertaken to delineate the source terms that can be expected in the use of a spray calcination/in-can melting vitrification system.

Data are presented of off gases from a variety of spray calciners and in-can melters. The off gases from the processing of defense, alternative, and power-reactor fuel wastes are characterized. Data from both radioactive and nonradioactive systems are discussed.

Data in this report will contribute to the solution of a major problem in the immobilization of high-level nuclear wastes, that is, the control of off gases.

EQUIPMENT DESCRIPTIONS

The effluent data presented here has been largely gathered from four spray calcination systems and two in-can melting systems. Although the design features of the systems are similar, there are some significant differences. A brief description of each is given.

SPRAY CALCINATION

A spray calciner is an externally heated right cylinder mounted vertically atop a product cone (see Figure 1). A bank of filters, also mounted atop the cone, is adjacent to the calciner chamber.

During operation the calciner chamber walls are heated to about 800°C by an external, multizone, resistance heated furnace. The liquid waste is metered and then pneumatically atomized in an internal- or external-mix spray nozzle and sprayed into the top center of the calciner chamber. The atomized liquid waste is sequentially evaporated, dried, and calcined (oxidized) as it falls through the calciner chamber. Heat is transferred to the droplets from the heated chamber walls via radiative and convective modes. The droplets are dried in a fraction of a second, producing calcine of typically less than 0.5% moisture. Calcine deposits on heat transfer surfaces within the calciner are prevented by the periodic operation of side-mounted vibrators.

On passing through the chamber, water vapor and atomizing air entrain 15% to 50% of the calcine particles and carry them to the sintered stainless steel filters. The solids and gases are separated by the filters with the gas passing on to the off-gas train. The solids collected on the filters are periodically removed by a pulse of blowback air. The dislodged calcine falls into the calciner collection cone and is discharged along with the calcine that falls directly from the calciner chamber.

The four spray calciners used to collect data were nonradioactive laboratory-, pilot-, and full-scale calciners, and a radioactive pilot-scale calciner.

FIGURE 1. Spray Calciner

Laboratory-Scale Spray Calciner

The laboratory-scale spray calciner (see Figure 2) calcines liquid waste at a nominal rate of 1 L/h or a maximum rate of 3 L/h, and at a nominal temperature of 800°C. The calciner chamber is a 12.7-cm-ID cylinder made of Inconel 601. The chamber is surrounded with five zones of half-section insulated, resistance heaters. The furnace assembly is surrounded by a stainless steel shell. Ten thermocouples are welded to the exterior wall of the calciner chamber. One of the thermocouples provides a signal that controls power input to the heaters. The other nine thermocouples record the temperature history.

The waste is sprayed into the calciner through an air-atomized nozzle. The nozzle is an internal mix unit with a spray orifice of 0.05 cm. The nozzle has a needle mounted on top of it to remove any solids plugging the orifice. An air-operated vibrator is mounted midway down the side of the calciner and is operated at intervals to remove calcine adhering to the furnace walls.

FIGURE 2. Laboratory-Scale Spray Calciner/In-Can Melter

The calcine and glass frit fall from the calciner chamber into the stainless steel calciner cone and then out of the calciner. The system is operated under 1.5 to 3.0 cm of Hg vacuum. Any gases generated by calcining are transferred through the filter chamber into the effluent control system. The filter chamber contains three stainless steel, sintered-metal filters that trap dust particles entrained in the gases. These filters are automatically pulsed with air to remove the dust particles whenever the pressure drop across these filters exceeds a set value.

Pilot-Scale Spray Calciner

The pilot-scale spray calciner, shown in Figure 3, is 53 cm in dia and 198 cm in length and has a nominal feedrate of 15 L/h. A two-zone, resistance-heated furnace surrounds the chamber and is insulated by a layer of high-temperature brick. Holes were bored through the brick layer to insert side mounted vibrators. Other pertinent data are listed in Table 1.

Full-Scale Spray Calciner

The full-scale spray calciner, shown in Figure 4, is 91.4 cm in dia and 322.6 cm long, and has a nominal feedrate of 200 L/h. The calciner has two sets of sintered stainless steel filters; one set has a nominal pore size of 65 μm , the other 10 μm . Table 2 gives other data on the full-scale spray calciner.

Radioactive Pilot-Scale Spray Calciner

The radioactive pilot-scale spray calciner is located in a radiochemical hot cell (shown in Figure 5), and has been extensively operated during two campaigns: the Waste Solidification Engineering Prototypes (WSEP) program (McElroy et al. 1972) and the Nuclear Waste Vitrification Program (NWVP).

The spray calciner is a 35.6-cm-OD cylinder with 0.95-cm wall thickness. The chamber is constructed of 310 stainless steel, which was chosen because of its excellent corrosion and oxidation resistance at high temperatures.

The spray chamber walls are heated to about 750°C by an external 3-zone resistance furnace. The furnace is rated at 20 kW per zone and is fired by a 240-V, 90-A power supply that provides a single phase to each zone.

FIGURE 3. Pilot-Scale Spray Calciner/In-Can Melter

TABLE 1. Pilot-Scale Spray Calciner Design Features

Spray Calciner Components	Design Specifications	
Calciner Chamber	ID	53 cm
	Height	198 cm
	Total heat-transfer area	3.3 cm ²
	Material	310 stainless steel
	Wall thickness	0.95 cm
Furnace	Type	Electrical resistance, 2 zones, 3 phase, 240 volts
	Control	Silicon controlled rectifier
	Power	80 kW (40 kW/zone)
	Heating elements	Nichrome
	Maximum temperature	1100°C
Atomizing Nozzles	Type	Pneumatic, internal mix
	Atomizing gas	Air
	Air cap material	303 stainless steel with or without 96% alumina insert
	Liquid orifice dia	0.64 cm
	Air cap orifice dia	0.64 cm
Filters	Total number	15
	Dia	5 cm
	Length	0.6 m
	Total surface area	2.39 m ²
	Mean pore size	65 μm
	Material	315 stainless steel, internally reinforced
Vibrators	Type	Pneumatic, dry lubricant
	Location	One on top and one on the side
	Size	1200 VMC (top) 1300 AC (side)
	Motive air pressure	70 psi (top)
		40 psi (side)

FIGURE 4. Full-Scale Spray Calciner/In-Can Melter

TABLE 2. Full-Scale Spray Calciner Design Features

Spray Calciner Components	Design Specifications		
Calciner Chamber	Material	310 Stainless steel	
	Dimensions	91.4 cm ID x 322.6 cm long	
Furnace	Number of Zones	4	
	Power	150 kW/zone 600 kW total	
	Electrical Supply	480 volts, 3 phase	
Calciner Cone	Material	340L Stainless steel	
	Dimensions	149.9 cm high x 92.7 cm wide x 149.9 cm long	
Off-Gas Filters	Material	10- μ m Filter Sintered 316 stainless steel	65- μ m Filter Sintered 316 stainless steel
	Pore size	10 μ m	65 μ m
	Number of Filter surface area	51	34
		7.44 m ²	6.82 m ²
	Dimensions	5.1 cm dia x 91.4 cm long	7 cm dia x 91.4 cm long

The liquid waste is pneumatically atomized into the top of the spray chamber with a commercially available, internal-mix, spray nozzle, which has been modified to accept a ceramic insert to control nozzle orifice erosion. The nozzle also includes a bellows-sealed, remotely operable cleanout needle, which is used to unplug the orifice remotely. Compressed air is used to atomize the liquid waste.

IN-CAN MELTING

The in-can melter is a furnace that is configured to accept a melting crucible (the canister) in which the melting of the calcine and glass-former mixture can take place (see Figure 6). The canister is used as the final container for storing the glass product; no product transfer is done.

FIGURE 5. Radioactive Pilot-Scale Spray Calciner/In-Can Melter

FIGURE 6. In-Can Melter

Although induction-heated furnaces have been used, the majority of the in-can melters developed at PNL have used resistance-heated furnaces. Process effluents are identical from either type of furnace. Two in-can melters have been used to gather the majority of the effluent data reported here: the pilot-scale in-can melter (see Figure 3) and the radioactive pilot-scale in-can melter (see Figure 5). The pilot-scale in-can melter was operated coupled to the pilot-scale spray calciner, and the radioactive pilot-scale spray calciner was operated coupled to the radioactive pilot-scale in-can melter. Off gases from the in-can melters exit through the spray calciner and sintered-metal filters.

Pilot-Scale In-Can Melter

The pilot-scale in-can melter is a single zone, resistance-heated furnace. It has a maximum operating temperature of 1100°C and is rated to 70 kW. The furnace can accommodate cans up to 40.6 cm in dia. The cans are suspended from a load cell and hung inside the furnace. There is an optional Hastelloy-X retort to provide a cover gas for the can. The furnace cavity is 140 cm long with a 49.5-cm-dia top opening. There are three Chromel-Alumel thermocouples in the furnace, one of which is used for power control.

Radioactive Pilot-Scale In-Can Melter

The in-can melter furnace is a 6-zone, resistance-heated furnace. Each zone is 35.6 cm high and has 15 kW of power. The furnace is fired by a 95-V, 50-A, 3-phase AC power supply. The design temperature for the furnace is 1000°C. A 38.1-cm-OD by 0.64-cm-thick wall Hastelloy-X susceptor tube is used in the furnace. Since the waste is self-heating due to radioactive decay, the furnace is cooled to maintain canister wall temperatures within material limits. Each zone of the furnace has a 2.5-kW cooling capacity at 2.83 m³/min, using air as the cooling medium.

PROCESS OFF-GAS SYSTEMS

Two process off-gas systems, one radioactive and one nonradioactive, have been extensively drawn upon to provide effluent data as related to spray calcination and in-can melting. In both systems, the first off-gas cleanup step is filtration through the sintered-metal filters. A general discussion, as described by Bonner (1976), follows.

Sintered Filters

Due to the small particle size of the spray-dried calcine, 15% to 50% of the solids are entrained in the water vapor and the atomizing air. Early experiments with various types of dust removal equipment led to the adoption of sintered, stainless steel filters. The general design of the filters presently used is shown in Figure 7.

FIGURE 7. Spray Calcliner Filter Assembly

During operation, solids filtered from the calcliner vapors are temporarily retained on the filter surface. With time the thickness of the deposited calcine increases and produces a corresponding increase in filter differential pressure. To remove the layer of calcine, a pulse of high-pressure air is directed into the filter from above. This reverse (blowback) air flow dislodges the calcine and allows it to fall to the calcliner cone below.

The sintered-metal filters that were used were made from appropriately sized metal powder that was formed into a sheet of suitable thickness and then

sintered. The sintered plate was then rolled into a reinforced tube and welded to a venturi. Each venturi was then welded into a plate to form a filter bank.

Varying the metal particle size can alter the filter pore size. Small pores provide the most efficient filtration, but also offer the largest resistance to vapor flow. However, the loss of efficiency with large pores is offset by the buildup of a calcine layer on the filter surface. This layer acts as a filtering media and produces a greater differential pressure.

Tests have been conducted with a combination of cyclones and filters and with various types of filters. As reported by Kaser and Moore (1966), a cyclone was used upstream of the filters. The filter cake was not easily removed by the pulsed blowback because only the finest particles reached the filter. These particles apparently formed an especially adherent filter cake.

Various filter media have been tested including porous alumina, fine woven wire, fine wound wire, sintered-fiber metal, and sintered-metal powder. The sintered-powder filters appear to exhibit the best compromise between filter efficiency and ease of cleaning by pulsed blowback air. Alumina filters had 10-mm-thick walls and pore sizes ranging from 10 to 100 μm . They were fragile and could not be cleaned effectively by pulsed blowback. Wire-wound and woven-wire filters were not as effective as sintered-powder filters, and sintered-fiber metal filters were expensive and operated at high differential pressure.

An excessive filter differential pressure caused by the buildup of calcine on the filter surface is prevented by using a blowback system to dislodge the filter cake. The blowback system is analogous to a jet ejector. The use of a venturi is intended to increase the entrainment of filtered gas by the blowback gas jet, thus decreasing the amount of external air required to clean the filters. Little information has been reported on venturi design; however, some work was done on the effects of venturi shape on blowback performance (Kaser and Moore 1966; Bjorklund 1976).

It is desirable to minimize calciner pressure surges caused by the pulses of blowback air. The variables that affect the magnitude of these surges are blowback pulse duration, blowback pressure, off-gas line flow resistance, and

the fraction of filters pulsed simultaneously. Experience has shown that a short 1/4-s pulse of 300°C air is as effective as a longer pulse. With this short pulse, blowback pressures of up to 530 cm of Hg can be used to clean one-fifth of the filters without pressurizing the calciner. In addition, past experience has shown that a 300-to 400-cm of Hg, 1/4-s pulse of heated air, delivered at intervals of 2 to 100 min, effectively cleans the filters.

Sintered stainless steel filters may not last indefinitely in continuous service due to gradual blockage of the filter pores. Since some of the calcine is smaller than the pore size of the filter, some particles penetrate the filter media and become lodged therein (Pall 1953). Calcine penetration is greatest at the filter surface, but is rapidly reduced when large particles bridge over the pores; this decreases the effective pore opening and acts as a filter precoat. During filter blowback the precoat is partially removed and some particles are again free to enter the filter media. Unfortunately, not all particles inside the filter media are removed during blowback, and a slow accumulation occurs. The rate of accumulation is dependent upon operating conditions and is eventually observed as an increase in minimum baseline differential pressure.

In the radioactive pilot-scale calciner, the sintered stainless steel filters were periodically washed to provide added filter permeability. Due to the low vacuum available for hot cell operations, the acceptable filter differential pressure was limited to about 1.9 cm of Hg, which was below the design value. Therefore, to prevent being forced to operate at reduced capacity, the filters were periodically washed with water or nitric acid. This cleansing was done by trickling water into the filter from above the venturi while activating the blowback cycle. Through this technique filter cake can be satisfactorially removed, and solids can be flushed from many of the filter pores. Improved filter cleaning can be obtained by using nitric acid instead of water--combining the force of physical removal with the chemical action of the acid.

After being placed in service, the pilot-scale spray calciner filter permeability^(a) declined as shown in Figure 8. This decline occurred as the layer of solids thickened and aged, and as some pores plugged. After about 120 to 150 h of operation, the permeability became somewhat stable. During a 500-h reliability test, filter permeability was actually observed to increase. However, under subsequent short runs in which the conditions varied widely, slightly poorer permeability was produced. Once filter permeability stabilized, it was noted that permeability was not reduced at higher filter face velocities even though the differential pressure was much greater. When the filter face velocity was later reduced, the differential pressure also returned

(a) Filter permeability is expressed in terms of actual filter face velocity in m/min per unit pressure differential in cm of Hg. Since flow through the filter pores is basically laminar flow, filter dew point is proportional to the throughput velocity. Thus, at a given temperature and solids-loading rate, permeability remains constant over a large range of face velocities and accurately indicates filter blinding.

FIGURE 8. Filter Permeability During Pilot-Scale Spray Calciner Operation

to its previous value. However, during operation, increased filter solids-loading did produce a temporary decrease in permeability, as shown in Figure 9. It is anticipated that during long-term operation, filter permeability will remain at 1.1 to 1.6 cm Hg differential pressure.

FIGURE 9. Filter Permeability

A filter cake, which is visually indistinguishable from the 150-h equilibrium coating, builds up on the filters after about 4 h of operation. The equilibrium coating varies randomly from 1/2 to 1-1/2 mm in thickness along the filter.

During a capacity test, filter permeability was observed to decrease rapidly when the temperature of the vapor reaching the filters dropped below the dew point. The decrease in permeability was indicated by filter differential pressure readings, and the calciner wall temperature was increased to heat the off gas. The hotter vapors effectively dried the filters, allowing the permeability to return to normal without decreasing or discontinuing the calciner feed.

Coupling a melter to the calciner has not affected the operation of the sintered-metal filters. The volume of gas leaving the melter is normally negligible when compared to the volume of gas leaving the calciner. Thus, the melter off gas has no noticeable effect on filter differential. Volatile components from the melter that are trapped in the filter cake comprise only a small portion of the solids collected there. Hence the volatile components are removed during filter blowback again without a noticeable effect on the filters. The concentration of some volatile waste constituents has been observed to be slightly higher in calcine that was removed from the filters. This observation indicates that these constituents are scrubbed from the vapors when the vapors pass through the filter-cake coating.

Nonradioactive Process Off-Gas System

The nonradioactive process off-gas system used is shown in Figure 10. The system following the sintered filters consists of an ejector venturi scrubber, a condenser, a packed scrubber, and a high-efficiency particulate air (HEPA) filter followed by a vacuum-producing fan. The entire system is operated at less than atmospheric pressure to insure that any gaseous leakage flows into the process. All liquid effluent streams in the system may be sampled. A variety of gas-sampling points are available.

The ejector venturi scrubber is a 316 stainless steel venturi with a 6-in. throat. It is designed to handle 14,160 L/m (500 acfm) of steam and 1,416 L/m (50 acfm) of NO_2 at 400°C and 4.7 cm Hg vacuum. The initial scrub solution is 182 L/m H_2O at 85°C and 310 cm Hg pressure. The venturi cools the gases to 60°C and is designed to remove 90% of the particles $1\text{ }\mu\text{m}$ or larger. When operating with a waste containing nitrates, the scrub solution reaches operating equilibrium at about 0.1M HNO_3 .

The condenser is a 304 stainless steel shell and tube heat exchanger. It's a single-pass down-draft unit, tube-side process with floating head construction and 14.2 m^2 of surface area. The shell side fluid is raw water at 13°C and 310 cm Hg pressure. The packed scrubber is a 304L stainless steel, packed-bed column. The packed bed is 0.25 m^3 of $2.54\text{ cm} \times 0.08\text{ cm}$ raschig rings. The column has a 2.54-cm cooling coil with 1.1 m^2 of surface area.

FIGURE 10. Flow Diagram for Non-Radioactive Process Off-Gas System

The HEPA filter is a 30-cm x 30-cm x 15-cm filter with a rated flow of $5.25 \text{ m}^3/\text{min}$ at a 2.5 cm Hg pressure drop. Gas is heated prior to entering the HEPA filter to raise the gas temperature above the dew point and prevent filter wetting.

Radioactive Process Off-Gas System

The radioactive process off-gas system is shown in Figure 11. This system was designed to provide three functions: 1) off-gas decontamination, 2) condensate concentration, and 3) high-level waste feed concentration. In this section, only off-gas cleanup will be discussed. The system consists of a quench scrubber, booster jet, condenser, evaporator with mist eliminator and condenser, fractionator, fractionator-condenser, fractionator distillate receiver, and scrubber.

The quench scrubber serves as the primary off-gas scrubber for the spray-calciner/in-can melter system. This scrubber is a 25.4-cm-dia, Schedule-20-pipe tower. It is made from 304L stainless steel and is packed with 2.5-cm

FIGURE 11. Radioactive Process Off-Gas System

pall rings of the same material. Two liquid distribution weirs, one near the top and a second at the midsection of the tower, serve to collect and redistribute scrub solution and condensate to the packing. Condensate from the fractionator distillate receiver is pumped to the top weir and, as it falls through the tower, it scrubs the rising gas stream. The scrub solution and the spray-calcliner condensate from the quench section of the tower are collected in a tank at the base of the tower and recycled by a pump to either the top or the bottom of the tower, depending on operating needs. This recycled liquid is cooled by passing it through a water-cooled heat exchanger. A constant liquid level is maintained in the collection tank by an overflow weir which allows drainage to the evaporator.

Located downstream from the quench scrubber is a booster jet or steam-jet assembly. This jet maintains the spray calciner/in-can melter system at the prescribed negative pressure. A condenser on the jet discharge line cools the gas and condenses the steam before it enters the evaporator.

The evaporator, constructed entirely of commercially pure titanium, is a medium-length-tube, thermosyphon-type designed to operate with a maximum-to-minimum operating volume ratio of 18:1. The evaporator has a tower with four stages of de-entrainment: 1) a simple chevron baffle at the bottom, 2) and 3) two stages of dry impingement caps in the center, and 4) a remotely replaceable mist eliminator at the top. At the maximum design boilup rate (500 L/h), the impingement velocities of stages 1, 2, and 3 are 11, 16, and 26 m/s, respectively. These velocities are sufficient for nearly 100% removal of aerosols of 25, 7, and 4 μm , respectively. The evaporator-condenser is a tube and shell down-draft-operated, water-cooled condenser with the process fluid on the tube side.

The totally titanium acid fractionator consists of a packed-tower distillation column surmounting a standard reboil tank. The top and bottom spheroid heads are partially reinforced for added strength with an extra thickness of titanium plate. The rectifying section of the fractionator tower is packed with 2.5-cm-dia, titanium raschig rings. The exhausting section includes a similarly packed section surmounted by the de-entraining sieve plate and the

integral reflux condenser. Special features of the fractionator are the remotely replaceable tube bundle in the reboiler and the de-entraining sieve plate with bypass provisions in the tower. The fractionator is designed for a liquid feed of up to 0.8M HNO_3 , an overhead fraction of 0.01M HNO_3 , and an acid concentration of up to 10M HNO_3 . The fractionator-condenser is the same type as the evaporator-condenser.

The process off-gas scrubber is a 1300-L tank surmounted by a packed scrubbing tower. A pump recycles the liquid scrub solution to the top of the tower at rates of up to 40 L/min. Gas flows of up to $11.8\text{ m}^3/\text{min}$ are acceptable.

WASTE DESCRIPTIONS

In relation to process effluents, three different types of wastes have been investigated 1) defense waste from the United States Government weapons program, 2) Thorex waste from the thorium-uranium alternative fuel cycle, and 3) Light Water Reactor (LWR) fuel-cycle waste.

Typical defense-waste composition and activity are shown in Tables 3 and 4. As can be seen from the composition, the waste is neutral (non-acidic) and the fission product content is low. Components of concern because of potential volatility and corrosion include mercury, the halogens and the organics.

TABLE 3. Defense-Waste Feed Composition

<u>Constituent</u>	<u>Concentration, g/L</u>
NaNO ₃	0.213
NaNO ₂	0.0693
NaAlO ₂	0.0374
NaOH	0.0315
Na ₂ CO ₃	38.3
Na ₂ SO ₄	0.0389
Na ₂ C ₂ O ₄	0.0158
Alk EDTA	9.79×10^{-4}
NaBO ₂	3.85×10^{-6}
Cl	8.62×10^{-4}
F	4.03×10^{-5}
H ₂ O	961
Fe(OH) ₃	23.5
UO ₂ (OH) ₂	3.60
CaCO ₃	3.18
Ni(OH) ₂	1.59
Hg(OH) ₂	1.42
C	2.43
MnO ₂	5.70
Al ₂ O ₃	0.0247
NiO	0.0013
SiO ₂	1.34
Insoluble Cl	0.795
Insoluble F	0.0419
Other	4.69 ^(a)

(a) Includes fission products and actinides.

TABLE 4. Defense-Waste Activities(a)

<u>Radionuclide</u>	<u>Activity, Ci/L</u>
^{137}Cs	23.10
^{90}Sr	26.70
^{106}Ru	0.98
^{129}I	Negligible
^{144}Ce	6.05
Other	<u>83.20</u>
Total	140.03

(a) Includes fission products and actinides.

Two Thorex fuel-cycle wastes are shown in Table 5. The Thorex wastes are nitric acid based wastes and contain significant quantities of fluorides. The TW-2 formulation contains aluminum, which acts as a fluoride complexant; TW-3 contains zirconium. Fluoride is potentially volatile and uncomplexed fluoride reaching the effluent cleanup system may cause unacceptable corrosion rates.

Compositions of a variety of wastes from the processing of LWR spent fuels are shown in Table 6. The concern with these acid-based wastes lies primarily with potentially volatile metals and their effect on the process off-gas system.

CALCINE CHARACTERISTICS

The particle-size distributions for typical, power-reactor, calcined wastes are shown in Figure 12. These distributions were obtained by U.S. Standard sieve analysis, Fisher subsieve analysis, Zeiss particle-size analysis, and Quantimet 720 projection-size distributions. Table 7 lists some typical physical properties of the calcined waste. Particle densities were measured by the helium displacement technique.

TABLE 5. Composition of Thorex Fuel-Cycle Wastes

<u>Inerts</u>	<u>TW-2, Nominal Molarity at 378 L/MTHM</u>	<u>TW-3, Nominal Molarity at 700 L/MTHM</u>
HNO ₃	2.0	2.00
Na	0.01	0.0054
Fe	0.18	0.41
Cr	0.02	0.011
Ni	0.009	0.0049
PO ₄	0.10	0.054
F	0.15	0.32
K	0.15	--
Al	0.36	0.0014
Zr	0.3	0.17
<u>Fission Products</u>		
Rb	0.021	0.011
Sr	0.040	0.022
Y	0.021	0.011
Zr	0.123	0.067
Mo	0.090	0.049
Tc	0.021	0.014
Ru	0.040	0.022
Rh	0.004	0.0022
Pd	0.010	0.0054
Te	0.013	0.0070
Cs	0.071	0.038
Ba	0.026	0.014
La	0.023	0.012
Ce	0.048	0.026
Pr	0.024	0.013
Nd	0.064	0.035
Pm	0.001	0.0005
Sm	0.011	0.0061
Eu	0.002	0.0011
Gd	0.002	0.046
<u>Actinides</u>		
Th	0.1	0.054
U	0.01	0.0054
Np	0.0004	0.0002
Pu	0.006	0.0032

TABLE 6. Compositions of Six Representative High-Level Radioactive Wastes as Liquids

	Concentration, Molarity at 378 L/MTU					
	PW-4b	PW-7	PW-7a	PW-7b	PW-7c	PW-8a
<u>Inerts</u>						
HNO ₃	1.0	2.0	2.0	2.0	7.0	2.0
Na	--	0.01	0.586	0.586	--	1.20
Fe	0.05	0.10	0.10	0.586	1.32	0.902
Cr	0.012	0.012	0.012	0.012	0.040	0.040
Ni	0.005	0.005	0.005	0.005	0.020	0.020
PO ₄	0.025	0.10	0.236	0.236	0.050	0.050
Gd	--	0.151	0.151	0.151	--	--
<u>Fission Products</u>						
Rb	0.010					
Sr	0.027					
Y	0.014					
Zr	0.106					
Mo	0.095					
Tc	0.022					
Ru	0.059					
Rh	0.010					
Pd	0.032					
Ag	0.002					
Cd	0.002					
Te	0.012					
Cs	0.054					
Ba	0.027					
La	0.024					
Ce	0.051					
Pr	0.023					
Nd	0.071					
Pm	0.0019					
Sm	0.014					
Eu	0.003					
Gd	0.002					
Concentration of fission products is the same for all six wastes.						
<u>Actinides</u>						
U	0.110	0.110	0.110	0.110	0.052	0.110
Np	0.0085	0.0085	0.0085	0.0085	0.0085	0.0085
Pu	0.0001	0.001	0.001	0.001	0.0005	0.0017
Am	0.0018	0.0018	0.0018	0.0018	0.0018	0.0018
Cm	0.0004	0.0004	0.0004	0.0004	0.0004	0.0004

FIGURE 12. Typical Spray-Calcine Particle-Size Distribution

TABLE 7. Physical Properties of Representative Calcined High-Level Wastes

Characteristics	Waste Calcine Types		
	PW-4b	PW-6	PW-7a
Density, g/cm ³			
Aerated bulk	0.85	0.41	0.69-0.92
Working bulk	0.97	0.48	0.87-1.04
Packed bulk	1.24	0.61	1.15-1.33
Particle	4.4	3.8	5.1
Compressibility	32%	33%	40%-31%
Angle of repose	42°	39°	43°-42°
Surface area, m ² /g	20	11	14
Nitrate content, wt%	1	19	2
Moisture content, wt%	1	1	1-4
Equilibrium aqueous slurry pH	4.5	5.0	--

SOURCE TERMS

The source terms generated during the calcination and vitrification of high-level wastes have been evaluated under four topical subjects: 1) volatile fission products, 2) particulate size and loading analysis, 3) gaseous constituents, and 4) other materials which include volatile nonfission products. Table 8 depicts the amounts and activities of the elements that may cause effluent problems in a facility which solidifies power-reactor wastes. As can be seen, the age of the waste is a very important factor; for example, Ru-106 with a half-life of 1.01 yr is the most predominant potentially volatile species in the high-level waste in terms of activity. Table 9 shows the allowable release rates as derived by Christian and Pence (1977), who chose 1/10 the maximum permissible release rate for use as a prudent minimum criteria. The decontamination factors are based on power-reactor wastes as defined in the table. The required decontamination factors for defense wastes would be lower because of the lower contained activities.

VOLATILE FISSION PRODUCTS

Constituents in the high-level wastes that are known to be volatile include tritium, krypton and iodine. Of the tritium present in spent fuel, 8% is assumed to be present in the high-level waste in the form of HTO (tritiated water). Because at present there are no special requirements for tritium control, no discussion on the subject will be given. The krypton content of high-level waste is extremely small. No krypton control will be necessary in a waste-solidification facility because the release will be negligible. The high-level waste from power-reactor fuel may contain a significant fraction of the iodine present in the spent fuels. Iodine in power-reactor waste probably will volatilize completely in any high-temperature process. The iodine in high-level defense waste will also probably all volatilize, although some may be chemically tied up with other materials, such as mercury.

TABLE 8. Critical Isotope Content of High-Level Waste (HLW)(a)

Isotope	$t_{1/2}$	Quantity	
		Ci/MTHM	g/MTHM
<u>Volatile</u>			
^3H	12.33 yr	33	3.5×10^{-3}
^{85}Kr	10.73 yr	8×10^{-3}	2.0×10^{-5}
^{129}I	1.59×10^7 yr	3×10^{-5}	0.2
<u>Potentially Volatile</u>			
^{79}Se	6.5×10^4 yr	0.34	4.9
^{99}Tc	2.13×10^5 yr	13	7.4×10^2
^{103}Ru	0.1084 yr	74	2.3×10^{-3}
^{106}Ru	1.01 yr	1.9×10^5	57
$^{103\text{m}}\text{Rh}^{(b)}$	56 min	74	--
$^{106}\text{Rh}^{(b)}$	29.9 s	1.9×10^5	--
$^{123\text{m}}\text{Te}$	0.3275 yr	1.7×10^{-2}	2.0×10^{-6}
$^{127\text{m}}\text{Te}$	0.298 yr	4.3×10^2	4.6×10^{-2}
^{124}Sb	0.1648 yr	0.7	4.0×10^{-5}
^{125}Sb	2.73 yr	5.9×10^3	5.7
$^{126\text{m}}\text{Sb}^{(b)}$	19.0 min	0.55	6.9×10^{-9}
$^{126}\text{Sb}^{(b)}$	12.4 days	0.54	6.5×10^{-6}
^{134}Cs	2.06 yr	1.2×10^5	91
^{135}Cs	2.3×10^6 yr	0.31	2.7×10^2
^{137}Cs	30.1 yr	9.3×10^4	1.1×10^3
<u>Potential Solids (Major activities, only)(c)</u>			
^{144}Ce	0.7787 yr	2.4×10^5	--
$^{144\text{Pr}}^{(b)}$	17.28 min	2.4×10^5	--
^{90}Sr	29 yr	6.1×10^4	--
$^{90\text{Y}}^{(b)}$	64.0 h	6.1×10^4	--
^{244}Cm	17.9 yr	7.0×10^3	--
TOTAL SOLIDS		1.1×10^6	6.5×10^4

(a) Fuel burnup is 28,700 MWd/MTHM. Waste age is 1-1/2 yr after discharge from reactor. Waste concentration is 379 L/MTHM (Reference: U.S. Dept. of Energy 1979).

(b) These isotopes are supported by longer-lived parents.

(c) In addition to those listed as potentially volatile (RuRh-106 and Cs-137).

TABLE 9. Maximum Permissible Radioactive-Release Quantities(a)

Isotope	Limiting MPC, $\mu\text{Ci/ml(b)}$	1/10 Maximum Permissible Release Rate at Stack, Ci/day(c)	10x Minimum Required Feed-to-Stack DF(d)	1/10 Maximum Allowed Volatility, for Complete Release, %
<u>Volatile</u>				
^3H	2×10^7	2×10^4	1×10^{-2}	8×10^3
^{85}Kr	3×10^{-7}	3×10^4	2×10^{-6}	5×10^7
^{129}I	2×10^{-11}	2	1×10^{-4}	8×10^5
<u>Potentially Volatile</u>				
^{79}Se	2×10^{-10}	9	3×10^{-1}	4×10^2
^{99}Tc	2×10^{-9}	2×10^2	3×10^{-1}	4×10^2
^{103}Ru	3×10^{-9}	3×10^2	2	6×10^1
^{106}Ru	2×10^{-10}	2×10^1	7×10^4	1×10^{-3}
$^{103\text{m}}\text{Rh(b)}$	2×10^{-6}	2×10^5	3×10^{-3}	4×10^4
$^{106}\text{Rh(b)}$	1×10^{-10}	9	1×10^5	7×10^{-4}
$^{123\text{m}}\text{Te}$	1×10^{-10}	9	1×10^{-2}	8×10^3
$^{127\text{m}}\text{Te}$	1×10^{-9}	9×10^1	3×10^1	3
^{124}Sb	7×10^{-10}	8×10^1	8×10^{-1}	1×10^2
^{125}Sb	9×10^{-10}	8×10^1	5×10^2	2×10^{-1}
$^{126\text{m}}\text{Sb(b)}$	1×10^{-10}	9	4×10^{-1}	2×10^2
$^{126}\text{Sb(b)}$	1×10^{-10}	9	4×10^{-1}	2×10^2
^{134}Cs	4×10^{-10}	3×10^1	2×10^4	4×10^{-3}
^{135}Cs	3×10^{-9}	3×10^2	8×10^{-3}	1×10^4
^{137}Cs	5×10^{-10}	4×10^1	1×10^4	7×10^{-3}
<u>Potential Solids (Major Activities in Addition to Those Above)</u>				
^{144}Ce	2×10^{-10}	2×10^1	9×10^4	--
^{144}Pr	1×10^{-10}	9	2×10^5	--
^{90}Sr	3×10^{-11}	3	2×10^5	--
^{90}Y	3×10^{-9}	3×10^2	2×10^3	--
^{244}Cm	3×10^{-13}	3×10^{-2}	2×10^6	--

(a) As derived by Christian and Pence (1977).

(b) Limiting MPC = smallest of maximum permissible limits for soluble, insoluble, and gaseous species.

(c) Assumes X/Q from stack-to-ground at site boundary = $1 \times 10^{-7} \text{ sec m}^{-3}$.

(d) DF = decontamination factor; feed rate: HLW from 6-2/3 MTU/day of fuel irradiated to 28,700 MWd/MTHM and cooled 1-1/2 years.

Elements that may be potentially volatile in a waste solidification process include: Ru, Cs, Sb, Te, Tc and Se. Based on Table 9, the volatile and potentially volatile elements of primary concern are ruthenium and cesium. The required decontamination factors are higher for ruthenium and cesium than for any other volatile or potentially volatile element, with the exception of ^{106}Rh , a daughter product of the ruthenium, but with a shorter half-life (^{106}Rh has a half-life of 29.9 s). In general then, it can be stated that if an effluent control system provides sufficient cleanup to control the ruthenium and cesium, it will also provide more than sufficient cleanup for the other volatile fission products.

Ruthenium is not merely a volatile metal. At temperatures about 800°C or above, the formation of gaseous RuO_4 takes place. At higher temperatures, the RuO_3 vapor species is formed by the reaction of O_2 or NO_2 with RuO_2 . The formation reactions become more thermodynamically favorable as the temperature increases. The formation of a stable, gaseous, complex, nitrosyl-nitrate form of ruthenium apparently occurs at temperatures about 800°C or below, and in the presence of nitric acid. The volatility of the complex form of ruthenium increases as the solidifier temperature decreases. Thus, control must be maintained by minimizing the volatility initially.

Therefore, attention has been placed on determining ruthenium and cesium losses from the spray calciner and in-can melter systems. This work has been done primarily in the pilot-scale spray calciner and in-can melter systems. A variety of feeds containing ruthenium and cesium were processed at several different temperatures. Table 10 gives the general results of the tests. Overall average total ruthenium and cesium losses were 0.045% and 0.042%, respectively, for all tests. Ruthenium losses varied from 0.001% to 0.16%, and cesium losses varied from "not detectable" to 0.132%. Correlations between volatility and H^+ content, or volatility and operating temperatures were not possible due to the large number of variables, except for run number DSS-29. Half of this run was made with 2M H^+ and half with 6M H^+ . No differences in volatilities were noted in either half.

TABLE 10. Pilot-Scale Spray Calciner/In-Can Melter Tests

Run Number	Feed	H ⁺	Feed % ^(a)		Temperature, °C	% Lost to Process Off-Gas		
			Ru	Cs		Ru	Cs	Other
DSS-29 ^(b)	PW-8a-2	2.6M	11	100	750-800	0.029	0.045	--
DSS-33 ^(c)	PW-8a-2	2.2M	20	100	575	0.0075	0.0028	--
DSS-34 ^(b)	PW-7	--	10	100	775	0.0010	Not detectable	--
DSS-35 ^(b)	PW-4b	1.0M	100	100	740	0.0011	0.0018	--
DSS-44 ^(b)	PW-7c	--	10	100	800	0.16	0.087	--
DSS-48 ^(b)	PW-7c	--	100	100	800	0.011	--	--
DSS-49 ^(b)	PW-9	--	25	100	800	0.044	Not detectable	0.039 Te
DSS-52 ^(b)	PW-7a	--	100	100	800	0.023	--	--
DSS-58 ^(c)	PW-7a	3.75N	30		800	0.011 ^(d)	--	--
DSS-60 ^(c)	PW-8	5M	100	100	750	0.018	0.01	--
DSS-61 ^(c)	TW-2	2M	--	100	750	--	0.132	--
DSS-62 ^(c,f)	PW-8	5M	100	100	750	0.084 ^(e)	0.013	
DSS-63 ^(b)	PW-4-7	5.5N	100	--	660-840	0.144	--	0.042 Sr

(a) Feed % is percent of defined flowsheet content used in the given run.

(b) Spray calciner data only.

(c) Spray calciner (SC) connected to in-can melter (ICM).

(d) Not all volatile; run started with clean filters, see effluent treatment section.

(e) Ru plateout seen in connecting section between SC and ICM.

(f) Duplication of DSS-60 except Si metal added.

A number of the runs were made with the in-can melter coupled to the spray calciner. During these runs, when the volatilities were compared to volatilities during runs with the spray calciner only, no differences were detected. This similarity is expected and is comparable to Gray's (1976) determination

of $7 \times 10^{-2}\%$ /h Ru and 1.5% Cs losses from borosilicate glasses. In the in-can melter, a cold cap of unmelted calcine and glass-former materials rests on top of the melt surface and condenses many of the volatile materials. Thus, the in-can melting process actually gives far lower volatilities than those from an uncovered molten glass surface.

Volatile species' decontamination factors for the spray calciner/in-can melter system are shown in Table 11. The average ruthenium and cesium decontamination factors were 2.0×10^4 and 2.7×10^4 , respectively, for all runs.

TABLE 11. Volatile Species Decontamination Factors (DF)

Run Number	Ru DF(a)	Cs DF	Other DF
DSS-29	3.4×10^3	2.2×10^3	--
DSS-33	1.3×10^4	3.6×10^4	--
DSS-34	1.0×10^5	1.0×10^5	--
DSS-35	9.2×10^4	5.6×10^4	--
DSS-44	6.2×10^2	1.2×10^3	--
DSS-48	8.8×10^3	--	--
DSS-49	2.3×10^3	(a)	2.5×10^3 (Te)
DSS-52	4.3×10^3	--	--
DSS-58	4.3×10^3	--	--
DSS-60	5.6×10^3	1.0×10^4	--
DSS-61	--	7.6×10^2	--
DSS-62	1.2×10^3	7.7×10^3	--
DSS-63	7.0×10^2	--	2.4×10^3 (Sr)

(a) No detectable volatile loss.

PARTICLE SIZE ANALYSIS AND PARTICLE LOADINGS

Penetration of the sintered stainless steel filters by the calcine is a source of fission products in the off-gas system. Because the filter pores are larger than the calcine particles, some calcine can pass through the filter.

The buildup of a calcine filter cake provides the filter efficiency required during spray calciner/in-can melter operation. With new or recently cleaned filters, an average decontamination factor^(a) of about 700 is obtained over the first few hours of operation. Average decontamination factors of up to 13,000 have been obtained in the pilot-scale spray calciner (Bonner, Blair, and Romero 1976). Overall average decontamination factors are 10^3 to 10^4 .

The size distribution of entrained calcine was studied because of the importance of the distribution in relation to the filtration of fission products from the calciner off-gas system. The study was performed using a classical aerosol scattering spectrometer to determine the distributions. The spectrometer uses a 5-mW, He-Ne, high-order, multi-mode laser and silicon photodiode detectors. An 11-element, high-resolution imaging system in the collection optics allows for particle trajectory analysis as well as light gathering. The scattered light from the laser is collected and reimaged within a dark field at 10x magnification or greater. The transmitted laser beam is dumped at a central stop on the first lens element. A masked beam-splitter derives two signals, which, in conjunction with double-pulse height analysis, provide a means of determining a particle's position as well as the center of the laser beam; this region has an area of 0.018 mm^2 . A 10/1 accelerator produces a flow rate of 6.15 m/s intersecting a portion of the laser beam 3 cm long. The sample volume is positioned at the center of the flow. The output from the spectrometer is recorded with a digital data-acquisition system.

The output from the digital data-acquisition system is automatically transferred to computer disc memory. Since the data-acquisition system outputs sets of data acquired in a batch mode, a large number of batches are stored on the disc. A data analysis program is then used to normalize and average the data sets. Gas flow rates and sampling time intervals are then input and the program calculates masses, particle counts, and mass percentages

(a) Decontamination factor is defined here as the ratio of the weight of solids material entering the calciner to the weight of the material leaving the sintered stainless steel filters.

as functions of particle size ranges. The program then plots all available data. The size range of particles that could be analyzed is shown in Figure 13 overlaid on the entire particle size distribution.

The majority of particle size data was taken during the operation of the pilot-scale spray calciner. The data from run DSS-49 will be discussed here. Data from other runs are given in the Appendix. No major differences were detected between operation with defense waste and operation with power reactor waste. In addition, data from the full-scale spray calciner were not significantly different from pilot-scale spray calciner data. The data discussed here are typical of all data taken.

Particle sizes were analyzed by isokinetically pulling a side stream sample from the off-gas line leaving the spray calciner sintered filter plenum. The plenum is a common area where all filters exhaust to the off-gas line. When the sample was taken, the spray calciner was being operated at a feedrate of 15 L/h using PW-7a waste. The gas temperature was 210°C; the spectrometer and sample lines were also operated at 210°C to prevent any temperature effects. The sample stream volume was 0.77 m³/min at standard conditions; 12.3 cm³/min was actually detected by the laser beam. During this time, the sintered-metal filters were blown back by 1/4-s pulses of air (at 520 cm Hg) every 15 min. The barrel vibrators operated for 3 s every 2 min.

Figures 14 through 19 show a set of typical size distributions obtained from the analysis of the side stream sample. Figure 14 shows the particle distribution in the size range of 0.35 to 0.755 µm and shows size distribution averaged over a number of runs. The time interval was normalized to 100 s. The numerical particle loading in the off gas was quite high, 1.59×10^7 particles/m³. Using a weighted average particle diameter of 0.43 µm (as was found in this analysis), and assuming a particle density of 4 g/cc³, a mass loading of 2.56×10^{-6} g/m³ was obtained.

In the size range of 0.50 to 2.75 µm, particle loadings of 3.0×10^7 /m³ were seen. The weighted average particle diameter for this range was 0.84 µm, which gives a mass loading in this range of 3.71×10^{-5} g/m³. The size distribution for this range, with a normalized time interval of 5 min, is shown in Figure 15.

FIGURE 13. Typical Pilot-Scale Spray Calciner Particle Size Analyzer Range

FIGURE 14. Typical Pilot-Scale Spray Calciner Particle Size Distribution from 0.35 to 0.755 μm (a)

(a) Averaged data. Time interval normalized to 100 s.

FIGURE 15. Typical Pilot-Scale Spray Calciner Particle Size Distribution from 0.50 to 2.75 μm (a)

(a) Averaged data. Time interval normalized to 5 min.

FIGURE 16. Typical Pilot-Scale Spray Calciner Particle Size Distribution from 1.00 to 7.75 μm (a)

(a) Average data. Time interval normalized to 10 min.

Figure 16 shows the distribution of particles in the 1.0- to 7.75- μm range. Loadings of 2.67×10^6 particles/ m^3 were seen for this group. Using a weighted average particle diameter of 1.54 μm , the mass loadings in the off gas

FIGURE 17. Typical Pilot-Scale Spray Calciner Particle Size Distribution from 2.0 to 20.0 μm (a)

(a) Averaged data. Time interval normalized to 10 min.

were determined to be $2.05 \times 10^{-5} \text{ g/m}^3$. In the largest size range of 2.0 to 20.0 μm , 2.11×10^5 particles/ m^3 were seen. The weighted average particle diameter was 3.16 μm . The mass loading was $1.41 \times 10^{-5} \text{ g/m}^3$. Figure 17 shows the size distribution.

The data for the four size ranges were integrated by normalizing the time interval and the band width. This was done by dividing the observed particle count by the individual size channel width. Figure 18 gives the integrated multi-range data. Overall particle loadings in the off gas for the size range of 0.35 to 20.0 μm was 4.18×10^8 particles/ m^3 , with a mass loading of $8.00 \times 10^{-5} \text{ gm/m}^3$. These measurements do not include material smaller than 0.35 μm . However, the mass percent distribution shown in Figure 19 indicates that the majority of the mass was centered around the 1.0- to 2.0- μm range, trailing off toward the 0.5- μm range. Thus, from the standpoint of mass, the

FIGURE 18. Typical Pilot-Scale Spray Calciner Overall Particle Size Distribution from 0.32 to 20.0 μm (a)

(a) Time interval normalized to 30 s.

FIGURE 19. Typical Pilot-Scale Spray Calciner Mass Percent Distribution

particles smaller than $0.35\text{ }\mu\text{m}$ were insignificant. Based on the particle size data, the gross solids de-entrainment efficiency of the sintered filters was 99.999%.

Particulate data in the Appendix includes pilot-scale spray calciner runs DSS-47, 49, 50 and 51. Table 12 gives the operating conditions for the runs. The sintered filters were cleaned prior to run DSS-49 and Figure 20 shows the effect. The mass distribution is skewed toward the larger-sized particles.

TABLE 12. Spray Calciner Operating Conditions During
Particulate Analysis

<u>Run Number</u>	<u>Feed Type</u>	<u>Feed Rate, L/h</u>	<u>Calciner Temperature, °C</u>	<u>Filter Temperature, °C</u>
DSS-47	Defense	15	850	445
DSS-49	PW-9	15	800	350
DSS-50	Defense	15	600	272
DSS-51	Defense w/Glass Formers	15	700	300

Particulate penetration data from the full-scale spray calciner have also been obtained. At the time the samples were drawn, the calciner was being operated at 250 L/h with simulated defense waste. The temperature of the calciner was 780°C and the filters were at 330°C . The filters being used had a nominal (98%) particle removal rating of $65\text{ }\mu\text{m}$.

Figures 21 through 24 show the data from the full-scale spray calciner. The mass loadings given in Table 13 were found using the weighted average particle diameters described earlier and particle densities of 4 g/cc . The particle count in the smallest size range was by far the highest; the very small size of the particles accounts for the low mass loading.

Since it appeared that a large portion of the particles was being released during filter blowback and vibrator operation, a sample was taken with both filter blowback and vibrator off. The results, shown in Figure 25, indicate that only about one-third of the number of particles detected during normal

FIGURE 20. Mass Distribution, Off Gas from Pilot-Scale Spray Calcliner With Clean Filters

operation could be accounted for. In the normalized time interval of 1 min, 10,613 particles were seen in the range of 0.32 to 0.755 μm. The loadings were 6.97×10^5 particles/m³ and 5.47×10^{-8} gm³.

Essentially no particles larger than about 0.5 μm were found in the off gas when the blowback and vibrator were not operating. Greater particle penetration of the filter was caused by the blowback than was caused by the vibrators. This penetration may occur because as the blowback cleans the filters, some particles pass through the filter before the filter cake builds up again.

The data from the four size ranges were integrated into one, as shown in Figure 26. This was accomplished by normalizing all observed counts to a common time and a common band width by dividing the observed count by the individual size channel width. Overlap between channel ranges was accounted for and corrected. There was a large amount of scatter in the low count or large particle end of the ranges, but there was a definite cutoff between 0.3 and 0.4 μm.

FIGURE 21. Full-Scale Spray Calciner Off-Gas Particle Size Distribution from 0.32 to 0.755 μm ^(a)

^(a) Averaged data. Time interval normalized to 1 min.

FIGURE 22. Full-Scale Spray Calciner Off-Gas Particle Size Distribution from 0.5 to 2.75 μm^(a)

(a) Averaged data. Time interval normalized to 10 min.

TABLE 13. FSCC-9 Mass Loadings

Size Range, μm	Time Interval, min	Particle Count, (m ⁻¹)	Mass Loading, g/m
0.32 to 0.755	10	2.2×10^6	1.7×10^{-7}
0.5 to 2.75	10	1.3×10^4	2.3×10^{-8}
1.0 to 12.25	10	1.8×10^3	1.2×10^{-8}
2.0 to 20.00	10	1.7×10^2	1.1×10^{-8}

FIGURE 23. Full-Scale Spray Calciner Off-Gas Particle Size Distribution from 1.0 to 12.25 μm (a)

(a) Averaged data. Time interval normalized to 10 min.

The particulate data show that the particles penetrating the sintered filters can account for a significant portion of the semivolatiles lost from the calciner to the off-gas system, but the majority of the mass penetrating the filters is in a size range that can be controlled.

GASEOUS CONSTITUENTS

The gaseous constituents that have been monitored in the spray calciner/in-can melter off gas include carbon monoxide (CO), carbon dioxide (CO_2), nitrogen oxide compounds (NO and NO_2), oxygen (O_2), nitrogen (N_2), and water (H_2O). Two instruments were used to monitor the gaseous constituents: a gas chromatograph (GC) and a nitrogen oxide analyzer.

FIGURE 24. Full-Scale Spray Calciner Off-Gas Particle Size Distribution from 2.0 to 20.0 μm^(a)

(a) Averaged data. Time interval normalized to 10 min.

The GC uses two packed columns: a 305-cm x 0.32-cm (10-f x 1/8-in.) poropak QS and a 183-cm x 0.32-cm (6-f x 1/8-in.) molecular sieve 5A with a dual thermal conductivity detector system. The columns are connected to the sample ports and the calibration gases via automatic valves as shown in Figure 27. Gas data are obtained by integrating "peaks", which are variations in the thermal conductivity of the gases passing through the detector. Quantitative data come from comparing the peak areas of the unknown gases to those of known calibration gases. The NO_x monitor functions by measuring the intensity of light generated from the chemilumnescent reaction of nitric oxide with ozone:

FIGURE 25. Full-Scale Spray Calciner Off-Gas Particle Size Distribution from 0.32 to 0.755 μm (a)

(a) Averaged data. Time interval normalized to 1 min. No filter blowback on vibrator operation.

FIGURE 26. Full-Scale Spray Calciner Integrated Off-Gas Particle Size Distribution from 0.32 to 20.0 μm (a)

(a) Averaged data. Time interval normalized to 30 s.

FIGURE 27. Gas Chromatograph Valving System

The intensity of the light generated is proportional to the concentration of the nitric oxide. If the concentration of NO_x is desired, the sample flow is routed through a stainless steel converter where nitrogen dioxide and other nitrogen compounds are converted to nitric oxide:

Gaseous data are presented from three operations: a full-scale spray calciner run, a full-scale spray calciner/in-can melter run, and a laboratory-scale spray calciner run. The full-scale spray calciner operation was with PW-7a feed. The calciner chamber wall temperature was 600°C and the feed-rate was 240 L/h. The samples were taken downstream of the sintered filters. The gas analyses are shown in Table 14. The NO_x monitor was not operated during this run.

A second full-scale spray calciner/in-can melter operation lasted for a period of five days. The feed was defense waste fed at 245 L/h. The calciner was operated at 775°C . Table 15 gives the mean gas data from the run and Table 16 gives detailed run data for all of the samples.

Two runs were made in the laboratory-scale spray calciner to compare nitric oxide and nitrogen dioxide quantities, one at the calciner furnace set point of 750°C and one at 850°C . The feedrate for both runs was approximately 1.7 L/h, and the feed was PW-7a. The results are shown in Tables 17 and 18.

POTENTIALLY VOLATILE NON-FISSION PRODUCTS

Fluoride is a potentially volatile non-fission product in Thorex fuel-cycle wastes and in some defense wastes. The primary potential problem caused by volatile fluoride is corrosion of the off-gas system and the sintered filters. The laboratory-scale spray calciner, the pilot-scale spray calciner/in-can melter and a laboratory-scale glass-melter crucible (constructed for volatility testing with TW-2 waste glass) were used to investigate fluoride volatility from simulated Thorex fuel-cycle wastes. Two waste types, TW-2 and

TABLE 14. Full-Scale Spray Calciner Gas Concentrations

Component	Concentration, g/L ^(a)				Mean Volume %
	Sample 1	Sample 2	Sample 3	Sample 4	
CO ₂	9.51 x 10 ⁻³	7.57 x 10 ⁻³	1.18 x 10 ⁻²	7.62 x 10 ⁻³	0.649
H ₂ O, NO _x ^(b)	6.40 x 10 ⁻³	8.83 x 10 ⁻³	9.53 x 10 ⁻³	9.73 x 10 ⁻³	1.50
O ₂	0.228	0.223	0.230	0.222	22.1
N ₂	0.678	0.634	0.691	0.688	75.2
CO ^(c)	<4 x 10 ⁻⁵	.4 x 10 ⁻⁵	4 x 10 ⁻⁵	4 x 10 ⁻⁵	<0.005

(a) Measured at 100°C and 0.93 cm Hg vacuum.

(b) H₂O and NO_x elute as one peak and the concentrations listed assume the peak is all H₂O.

(c) Trace quantities of CO that approached the sensitivity limit of the gas chromatograph were measured.

TABLE 15. Five-Day Full-Scale Spray Calciner/In-Can Melter Mean Off-Gas Data ^(a)

Component	Mean Concentration, g/L	Standard Deviation	Mean Volume %
CO ₂	2.32 x 10 ⁻³	1.94 x 10 ⁻³	0.164
H ₂ O, NO _x	7.36 x 10 ⁻³	7.85 x 10 ⁻³	1.27
O ₂	0.214	5.10 x 10 ⁻²	20.7
N ₂	0.696	6.48 x 10 ⁻²	77.1
CO	2.57 x 10 ⁻⁵	2.28 x 10 ⁻⁵	0.0029

(a) Measured at 100°C and 0.93 cm Hg vacuum.

TW-3, containing different fluoride levels were tested. Figure 28 shows the spray calciner system used and Table 19 gives the results from the laboratory-scale spray calciner test.

The pilot-scale spray calciner was operated coupled directly to the pilot-scale in-can melter. The feed was simulated TW-2. The average flow rate was 20 L/h, for 7.5 h. The in-can melter was held at a melt temperature of about

**TABLE 16. Full-Scale Spray Calciner/In-Can Melter 5-Day
Run Off-Gas Data(a)**

Before Venturi	After Venturi	After Packed Tower	Off-Gas Flow M ³ /min	Concentration CO ₂ g/L	Concentration H ₂ O, NO ₂ g/L	Concentration O ₂ g/L	Concentration N ₂ g/L	Concentration CO g/L
x			1.92	9.12E-4	2.13E-3	0.237	0.716	--
x			2.14	5.23E-4	2.45E-3	0.244	0.723	--
x			1.82	5.07E-4	1.35E-3	0.232	0.695	--
x			0.63	5.49E-4	8.23E-3	5.34E-2	0.717	--
x			--	2.41E-3	1.99E-3	0.221	0.721	--
	x		0.73	4.18E-3	4.18E-3	0.194	0.700	3.62E-5
	x		1.05	7.98E-3	5.72E-3	0.197	0.711	3.41E-5
x			--	8.85E-4	1.60E-3	0.227	0.708	--
x			1.17	9.82E-4	2.87E-2	--	0.341	--
		x	1.23	4.95E-3	4.42E-3	0.245	0.727	--
		x	1.23	3.71E-3	6.4E-3	0.241	0.691	1.03E-5
		x	1.27	3.24E-3	7.53E-3	0.236	0.659	1.72E-5
		x	1.48	4.61E-3	7.68E-3	0.245	0.726	4.02E-5
		x	1.57	--	3.08E-3	0.188	0.725	1.63E-5
x			1.57	--	1.98E-3	0.215	0.727	8.91E-7
x			1.25	--	2.15E-3	0.183	0.729	--
x			1.64	5.03E-4	2.45E-2	7.66E-2	0.709	--
x			1.51	5.39E-4	2.48E-2	5.94E-2	0.732	3.49E-6
x			1.20	5.85E-4	1.52E-3	0.242	0.692	--
	x		1.92	4.55E-3	7.19E-3	0.236	0.652	1.08E-6
		x	2.17	3.74E-3	8.01E-3	0.237	0.705	--
		x	1.85	3.62E-3	8.59E-3	0.228	0.646	--
		x	2.06	2.88E-3	9.60E-3	0.242	0.723	--
		x	2.27	2.55E-3	8.91E-3	0.229	0.655	1.6E-5
		x	1.67	4.56E-3	9.40E-3	0.184	0.676	4.79E-5
		x	2.30	2.53E-3	9.21E-3	0.232	0.700	1.66E-5
		x	1.78	2.68E-3	--	0.235	0.708	--
		x	1.61	5.8E-4	7.46E-3	0.240	0.721	--
		x	1.72	--	5.92E-3	0.239	0.719	1.48E-5
		x	1.73	5.71E-4	5.96E-3	0.239	0.717	--
		x	1.55	4.44E-3	5.99E-3	0.242	0.722	1.72E-5
x			1.21	5.37E-4	1.45E-3	0.242	0.718	--
	x		1.01	5.5E-4	1.28E-3	0.239	0.719	--
x			1.78	5.17E-4	6.81E-3	0.235	0.709	--
x			1.62	--	6.76E-3	0.235	0.698	--
x			--	5.32E-4	4.05E-2	--	0.707	--

(a) At 100°C and 0.93 cm Hg vacuum.

1050°C for 11 h. Samples of glass were removed from the top, middle, and bottom of the glass canister and analyzed for fluoride. The wt% fluoride was 0.12, 0.18, and 0.60, respectively. The higher fluoride content in the bottom sample was expected since a second phase other than glass formed. This formation was caused by control problems with the frit feeder, which resulted in the

TABLE 17. Laboratory-Scale Spray Calciner Data

	Mean Volume %, Air	Mean Volume %, Condenser Outlet(a)	Enrichment over Air, %
NO	--	0.508	--
NO _x (b)	--	0.700	--
NO ₂	--	0.208	--
CO ₂	0.0484	0.0811	68
H ₂ O(c)	0.271	5.81	2044
O ₂	20.8	19.1	-8.2
N ₂	78.7	74.1	-5.8
CO	--	0.012	--

(a) Calciner operated at 750°C.

(b) Assume NO_x = NO + NO₂.

(c) Obtained by difference.

TABLE 18. Effect of Calciner Temperature Set-Point on NO_x Production

Component	Calciner Set-Point 750°C, ppm	Calciner Set-Point 850°C, ppm	Concentration Increase, %	Condenser Outlet, 850°C, ppm
NO	5,075	6,680	32	6,500
NO _x (a)	7,000	10,900	56	11,400
NO ₂	1,925	4,220	119	4,900

(a) Assume NO_x = NO + NO₂

calcine-to-frit ratio of 1:4 being exceeded in this portion of the canister. An overall fluoride mass balance gives an expected glass concentration of 0.16 wt%, which is similar to the top and middle fluoride concentrations. Fluctuations between glass samples prohibit estimates of fluoride loss from glass analyses. However, the analyses of fluoride in condensate samples indicate a loss of only 2%.

FIGURE 28. Laboratory-Scale Spray Calciner

TABLE 19. Fluoride Losses from the Laboratory-Scale Spray Calciner

Feed Type	Run Time, h	Average Feedrate, L/h	Average Volatility, %	Volatility Range, %
TW-2	7.9	0.83	3.5	0-9
TW-2	48.3	1.05	3	0.5-9
TW-3	8	0.75	5	3-7
TW-3	8	1.5	5	3-7

The laboratory-scale crucible was half-filled with powdered TW-2 glass. An argon gas flow was maintained over the crucible to prevent clogging of the tubes by precipitation of volatiles. A vacuum of 1.9 to 3.7 cm Hg was maintained throughout the test, as in the full-scale process. The off gas was

bubbled through two successive aqueous traps; the first contained 0.35M NaOH and the second contained distilled water. The crucible furnace was held at 1200°C for 48 h, and then was furnace-cooled.

The calcine used in the crucible melt test was produced from the 50-h laboratory-scale spray calciner run. Table 20 lists the glass composition used in the melt test.

TABLE 20. Glass Composition for TW-2

<u>Constituent</u>	<u>In Glass, wt%</u>
TW-2-1 Calcine	20.0
Al ₂ O ₃	1.7
SiO ₂	41.9
B ₂ O ₃	14.4
Na ₂ O	8.6
CaO	3.2
BaO	3.2
ZnO	2.5
K ₂ O	2.5
Li ₂ O	2.0

The caustic and aqueous-trap solutions were analyzed for fluoride using the Amadac-F colorimetric method. Both solutions were also analyzed using an inductively coupled plasma-emission spectrometer to detect the presence of metallic elements. Table 21 lists the total weights of each element found in each solution. These quantities of off gas constituents were collected from 563 g of total glass containing 20% TW-2 calcine by weight.

Based on these fluoride analyses, volatility from glass melting at 1200°C is about 0.2%. Other elements besides sodium that were found in appreciable quantities in the caustic scrub were B, Al, Ca, K, Si, and Mo. Of these, the only fluorides that would be expected to be potentially volatile would be boron and silicon. However, if boron and silicon had volatilized, the

fluoride analyses would have been much higher than 3.0 mg. It is possible that these elements were added as impurities with the NaOH, or that they entered the scrubber as particulates.

TABLE 21. Elements Found in Off-Gas Traps

<u>Element</u>	<u>Caustic Trap, mg</u>	<u>Aqueous Trap, mg</u>
F	3.0	0.0
Al	0.91	0.03
B	2.95	0.12
Ca	0.45	0.41
Fe	0.00	0.00
K	27.85	1.32
Li	0.001	0.000
Mg	0.08	0.124
Na	1000	1.19
P	0.042	0.003
Si	35.6	0.003
Ag	0.11	0.003
Co	0.012	0.017
Cu	0.079	0.076
Mn	0.008	0.008
Mo	0.16	0.00
Th	0.000	0.007
Ti	0.009	0.000
Tl	0.000	0.000
U	0.000	0.022
Zn	0.029	0.039
Zr	0.036	0.000

EFFLUENT TREATMENT

A variety of off-gas cleanup devices may be used to accomplish the necessary cleanup of entrained particulate and volatilized fission products. According to the cleanup requirements mentioned earlier, a device that effectively controls ruthenium (the worst case volatile species), will sufficiently control other potentially volatile species such as Cs, Se, Tc, Te, and Sb.

A list of typical decontamination factors for various types of cleanup devices, as compiled by Christian and Pence (1977) from a variety of sources, is given in Table 22. Operations in the nonradioactive off-gas system have yielded the decontamination factors listed in Tables 23 and 24.

TABLE 22. Typical Decontamination Factors Across Off-Gas Cleanup Devices

Component	Decontamination Factors			
	Particulates	Volatilized Ru	NO ₂	NO
Cyclone	10	1	1	1
Venturi Scrubber	100 to 600	10	2	1
Tube and Shell Condenser	10 ² to 10 ³	2 x 10 ²	2	1
NO _x Absorber	10	10	5	1
Brink Fiber Mist Eliminator	10 ²	1	1	1
Packed Spray Tower	10 ³	10 ²	4	1
NO _x Converter	2	3.8 x 10 ²	10 ²	10 ²
Ruthenium Sorber:				
Silica Gel	8	10 ³	1	1
Fe ₂ O ₃ on Glass	2	(1 to 5) x 10 ²	1	1
Sintered Metal Filter	10 ³	1	1	1
HEPA Filter	10 ³	1	1	1

TABLE 23. Nonradioactive Off-Gas System Ruthenium Decontamination Factors (DF)

<u>Run Number</u>	<u>Feed Type</u>	<u>Condenser DF</u>	<u>Venturi DF</u>
DSS-58	PW-7a	2.8	3.2
DSS-60	PW-8	2.9	2.3
DSS-62	TW-2	15.0	NA
DSS-63	PW-4b	3.8	36.3
DSS-44	PW-7c	1.2	NA
DSS-49	PW-9	1.3	NA

TABLE 24. Nonradioactive Off-Gas System Cesium Decontamination Factors (DF)

<u>Run Number</u>	<u>Feed Type</u>	<u>Condenser DF</u>	<u>Venturi DF</u>
DSS-60	PW-8	2.5	4.8
DSS-61	TW-2	5.0	NA
DSS-62	TW-2	4.2	NA
DSS-44	PW-7c	3.5	NA
DSS-49	PW-9	19.5	NA

Figure 29 shows typical condensate concentration following startup. The data shown are from run DSS-35, which used PW-4b feed. A relatively large amount of material from the spray calciner passes through the filters until the filters are caked. The concentrations then level off and hold constant. Typical off-gas system concentrations of elements from run DSS-49 are shown in Tables 25, 26 and 27. As seen from the data, decontamination factors obtained in nonradioactive testing for tube and shell condensers and venturi scrubbers are generally lower than those described by Pence and Christian (1977).

A discussion of the interesting fission product behavior in run DSS-63 follows. Run DSS-63 was made with PW-4b feed. The calciner was operated in the temperature range of 840⁰ to 660⁰C, averaging about 720⁰C. The off-gas system samples were analyzed for ruthenium and strontium,

FIGURE 29. Startup Condensate Concentrations

with the strontium being used as a measure of nonvolatile particulate loss from the system. The concentrations in the feed were: Ru - 6.00 g/L, and Sr - 2.18 g/L. Ruthenium volatility can then be determined by comparing ruthenium concentrations to strontium concentrations in the condensate. If the ratio is approximately three, as it was in the feed, then no detectable ruthenium volatility is present.

TABLE 25. Condensate Concentrations DSS-49, mg/L

Elapsed Time, h	Sr	Cs	Ru	Rb	Te	Mo
0	-----FEED ON-----					
1.4	0.31	0.50	0.01	0.05	0.09	0.30
2.4	0.40	1.7	0.36	0.19	0.25	1.4
3.4	0.44	1.9	0.41	0.20	0.36	1.6
4.4	0.42	1.6	0.48	0.18	0.41	1.6
5.9	0.38	1.5	0.48	0.16	0.37	1.5
7.4	0.37	1.1	0.37	0.12	0.35	1.3
8.4	0.38	1.1	0.32	0.11	0.34	1.4
9.4	0.34	1.0	0.35	0.10	0.32	1.2
10.4	0.32	0.86	0.22	0.08	0.34	1.2
11.4	0.27	0.77	0.23	0.07	0.28	1.1
11.9	0.24	0.63	0.22	0.07	0.25	0.9
12.1	-----FEED OFF-----					

TABLE 26. Venturi Scrub Concentrations DSS-49, mg/L

Elapsed Time, h	Sr	Cs	Ru	Rb	Te	Mo
0	-----FEED ON-----					
1.4	0.27	1.1	0.14	0.11	0.13	0.61
2.4	0.48	2.5	0.22	0.30	0.19	0.95
3.4	0.32	1.5	0.16	0.17	0.11	0.61
4.4	0.35	1.5	0.20	0.16	0.12	0.64
5.9	0.34	1.5	0.19	0.17	0.13	0.66
7.4	0.35	1.5	0.20	0.15	0.15	0.64
8.4	0.34	1.5	0.32	0.16	0.17	0.65
9.4	0.34	1.5	0.22	0.17	0.16	0.64
10.4	0.34	1.5	0.27	0.17	0.16	0.64
11.4	0.35	1.5	0.23	0.15	0.18	0.69
11.9	0.36	1.5	0.23	0.17	0.17	0.67
12.1	-----FEED OFF-----					

TABLE 27. Packed Scrub Concentrations DSS-49, mg/L

Elapsed Time, h	<u>Sr</u>	<u>Cs</u>	<u>Ru</u>	<u>Rb</u>	<u>Te</u>	<u>Mo</u>
0	-----FEED ON-----					
1.4	0.08	0.01	0.01	0.01	0.01	0.18
2.4	0.10	0.07	0.01	0.01	0.04	0.08
3.4	0.11	0.11	0.01	0.01	0.04	0.15
4.4	0.11	0.14	0.01	0.01	0.04	0.18
5.9	0.12	0.17	0.02	0.02	0.07	0.25
7.4	0.12	0.23	0.02	0.02	0.05	0.27
8.4	0.12	0.24	0.02	0.02	0.06	0.25
9.4	0.13	0.29	0.02	0.02	0.07	0.30
10.4	0.13	0.30	0.03	0.02	0.06	0.28
11.4	0.14	0.35	0.04	0.02	0.07	0.32
11.9	0.14	0.38	0.04	0.03	0.08	0.35
12.1	-----FEED OFF-----					

Figure 30 shows the instantaneous concentrations of ruthenium and strontium in the condensate during the run. The first peak shows the initial particulate penetration when starting up on "clean" filters. The second peak shows a period of ruthenium volatility which tapers off but does not stop during the remainder of the run. What initiated this volatility is not known, although it may have taken time for the off-gas system to equilibrate with the volatile ruthenium. A large vacuum (7.5 to 11.2 cm Hg) on the filters just prior to the sample may have caused a rise in the concentrations of ruthenium and strontium via increased filter penetration.

Figure 31 shows the average concentration in the condensate of ruthenium and strontium. The concentrations in the venturi scrubber, which was the next piece of equipment in the off-gas train, are shown in Figure 32. No gain above background was seen for the strontium concentration. No gains above background were seen for either ruthenium or strontium in the packed scrubber, the final stage of cleanup.

FIGURE 30. Instantaneous Ruthenium and Cesium Concentrations

The total percents of ruthenium and strontium that were lost from the spray calciner, based on the amounts found in the off-gas systems, were: Ru - 0.144%, and Sr - 0.042%. Of the ruthenium that was lost, 74% ended up in the condenser and 26% ended up in the venturi scrubber; no ruthenium was detected in the packed scrubber. Of the strontium that was lost, 62% ended up in the condenser and 38% ended up in the venturi scrubber; no strontium was detected in the packed scrubber.

FIGURE 31. Average Ruthenium and Strontium Condensate Concentrations

Ruthenium concentrations in the condensate from run DSS-58 show initial high losses during startup. Figure 33 shows the instantaneous ruthenium concentration in the condensate. Instantaneous losses were initially high and tapered off during the remainder of the run. The filters had been washed before this run, which accounts for the initial high loss. A large portion of the ruthenium found in the condensate can be accounted for during the initial operating period.

Another potential problem was the possibility of ruthenium plate-out in the sintered filters. The filter that was used for the 48-h TW-2 waste run in the laboratory-scale spray calciner was destructively tested to look for ruthenium plate-out within the media of the filter. The filter had been operated for 48 h with TW-2 feed. The filter was broken and a cross section was analyzed. The results, depicted in Figure 34, show a specimen current photograph of the filter interior, and prints of Fe, Ru, and Cs concentrations.

FIGURE 32. Venturi Scrubber Ruthenium and Strontium Concentrations

FIGURE 33. Instantaneous Ruthenium Concentration, Pilot-Scale Spray Calciner Run DSS-58

Specimen Current

Iron

Ruthenium

Cesium

FIGURE 34. Sintered Stainless Steel Filter Cross Section, 100X

The intensity of the light areas in the photographs is a measure of the amount of the material seen. It should be noted that only the white areas showing on the iron specimen photograph lie within the plane of focus (on all tests). The amounts of ruthenium and cesium are not significant; the spots showing on the photograph are only background noise. Analyses found no ruthenium or cesium concentrations greater than 0.5% in any 1- μ m-dia area.

Radioactive effluent system data obtained during two high-level waste concentration and vitrification operations at PNL are shown in Tables 28 and 29. In the process of concentrating and solidifying the high-level PW-8 type waste, more than 1.03×10^6 curies of beta-gamma and 4.14×10^3 Ci of alpha materials were processed. Since the radioactive waste was a nitric acid based solution, nitrogen oxide (NO_x) evaluations were also completed. The off-gas system sufficiently reduced the NO_x concentration from the solidification to the stack such that 5% opacity was never exceeded (5% is the visible opacity threshold). Prior to stack dilution, nitrogen oxide levels were low, generally in the area of 1000 to 2000 ppm.

Another source of radioactive off-gas data is the Waste Solidification Engineering Prototype (WSEP) program completed in the late 1960s (McElroy et al. 1972). Of all the runs completed in the WSEP program, only the final two runs, SS-12 and SS-13, were made with spray calciner and in-can melter hardware similar to that used in the nonradioactive tests. The operating conditions and resulting ruthenium losses are shown in Table 30. The ruthenium losses are believed to be high due to ruthenium deposits in the system from previous non-borosilicate glass operations.

Radioactive off-gas data was also obtained in the high-level waste research done by Y. B. Katayama (Mendel 1977). Katayama carried out the solidification process in an in-pot calciner; volatilities from that equipment would be expected to be somewhat higher than those from a spray calciner. High-level waste from the Zorita reactor was calcined at 500°C in a batch of 100 g. Ruthenium (^{106}Ru) losses were 0.05%. Cesium (^{137}Cs and ^{134}Cs) losses were 0.31%. Decontamination factors obtained across the calciner (no filters) were 2×10^3 and 3.2×10^2 for ruthenium and cesium, respectively.

Considering that the solidification was done in-pot and that no filtration was used, Katayama's data are comparable to the data obtained for the nonradioactive, simulated waste.

TABLE 28. Gross Activity Released to Stack During Radioactive Operation

Operation	Activity Released, Ci			Activity Concentration, Ci/cc		
	Alpha	Beta	Gamma	Alpha	Beta	Gamma
HLW Concentration #1 ^(a)	$<1.25 \times 10^{-7}$	$<3.48 \times 10^{-7}$	(b)	$<1.56 \times 10^{-15}$	$<4.27 \times 10^{-15}$	(b)
SC/ICM #1 ^(a)	$<4.1 \times 10^{-8}$	$<4.6 \times 10^{-8}$	(b)	$<1.5 \times 10^{-15}$	$<1.7 \times 10^{-15}$	(b)
HLW Concentration #2 ^(a)	$<1.7 \times 10^{-8}$	$<7.3 \times 10^{-8}$	(b)	$<6.4 \times 10^{-16}$	$<2.7 \times 10^{-15}$	(b)
SC/ICM #2	$<1.8 \times 10^{-8}$	$<7.3 \times 10^{-8}$	1.64×10^{-3}	$<6.5 \times 10^{-16}$	$<2.7 \times 10^{-15}$	9.5×10^{-16}

(a) During these spray-calcliner/in-can melter (SC/ICM) operations, a spent commercial fuel dissolution system was in operation and may have contributed to the activities.
 (b) Data not available.

TABLE 29. Radioactive Effluent System Minimum Decontamination Factors (DF)

Operation	DF	
	Alpha	Beta - Gamma
HLW Concentration #1	7×10^9	(a)
SC/ICM #1	2×10^{10}	(a)
HLW Concentration #2	1×10^{11}	(a)
SC/ICM #2	7×10^{10}	2×10^8

(a) Data not available.

TABLE 30. WSEP Spray Solidification Data

Run Number	Feed	Temperature, °C	Ru Lost to Process Off-Gas, %	System Ru DF
SS-12	PW-4m	730	1.9	5.3×10^1
SS-13	PW-4m	685	0.5	2.0×10^2

CONCLUSIONS

According to data obtained during calcination of nonradioactive, simulated waste, ruthenium and cesium losses from the spray calciner are small, on the order of $3.5 \times 10^{-2}\%$ and $3.4 \times 10^{-2}\%$, respectively. Calciner-melter and filter decontamination factors for ruthenium and cesium averaged 3.6×10^4 and 3.9×10^4 , respectively. Particulate decontamination factors of 10^3 to 10^4 have been obtained using sintered stainless steel filters. A significant portion of the ruthenium and cesium lost to the process off-gas system was due to particle penetration of the filters. The particles penetrating the filters have a mass distribution centering about a size large enough to control with available technology.

Processing wastes containing fluoride will probably volatilize a portion of the fluoride to the off-gas system, thus increasing the probability of corrosion problems.

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ACKNOWLEDGMENTS

Appreciation is extended to T. A. Nelson for his gas chromatograph and NO_x monitoring work, to J. T. Jeffs for the samples collected during many hours of operational time, and to F. T. Hara for his analytical expertise.

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APPENDIX
PARTICULATE SIZE DISTRIBUTIONS FROM
PILOT-SCALE SPRAY CALCINER

The material contained in this appendix describes the particulate size distributions from pilot-scale spray calciner operations as discussed in the section on Particle Size Analysis and Particle Loadings.

RUN NUMBER
DSS-47

RUN NUMBER
DSS-47

RUN NUMBER
DSS-47

RUN NUMBER
DSS-47

RUN NUMBER
DSS-49

RUN NUMBER
DSS-49

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